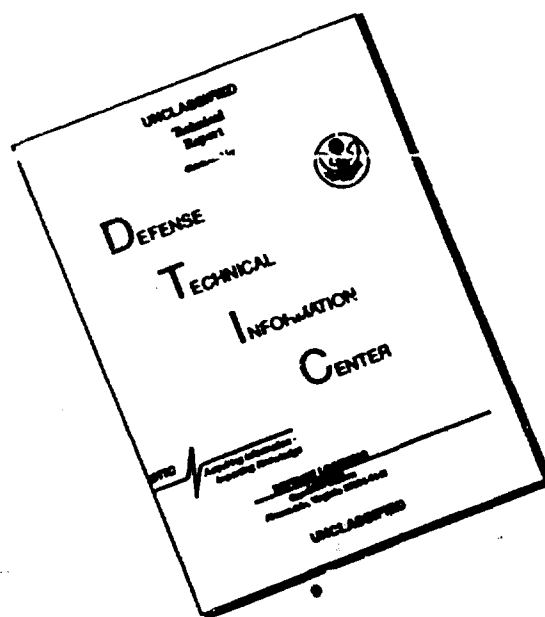# DISCLAIMER NOTICE

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Abstract

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This translation was prepared from an article originally published as follows: Pokhil, P. F., and L. D. Romodanova. O gorenii sostavov na osnove okislitelya perkhlorata kaliya i metallicheskikh goryuchikh v vakuume. IN: Akademiya nauk SSSR. Zhurnal fizicheskoy khimii, v. 39, no. 11, 1965, 2757-2759. The author cites works from which it is known that mixtures containing potassium perchlorates and organic fuels can burn flamelessly in a vacuum. He feels that it is of scientific interest to study the individual stages of the combustion of mixtures containing potassium perchlorate and metal fuels (tungsten, zirconium, and molybdenum) in a vacuum because, by means of a vacuum test, it is possible to determine whether the initial combustion stage of the mixture takes place in the condensed phase or whether the mixture burns only in the gaseous phase. Stoichiometric mixtures containing $KClO_4$ as oxidizer and W, Zn, Mo, and Ti as fuels were used by the author as research objects. Grains 5 mm in diameter were compacted to the maximum density. Seven tables present data such as results of the self-ignition temperatures of the mixtures in a vacuum and the sizes of the metal particles; surface temperatures of the mixtures during flameless combustion in a vacuum; results of the determined rate W of flameless combustion of the mixtures; results of the solid and gaseous phase analysis for flameless combustion in percentages of the intial batch. The author makes two conclusions: 1) The initial stage of combustion of every mixture occurs in the reaction layer of the condensed phase, i.e., on the surface of the fuel particles, with a total positive heat of reaction, and it ends in the generation of a smoke-gas combustible mixture which then burns in the region above the surface of the mixture until, under certain conditions, the final combustion products are formed. 2. Self-ignition of the mixtures occurs at a temperature at which the metal is in the solid state. There are two references.

FOREWORD

This is a translation of a Soviet article originally
published as follows:

THE COMBUSTION OF MIXTURES CONTAINING POTASSIUM PERCHLORATE AS OXIDIZER AND METAL FUELS IN A VACUUM

From works [1, 2], it is known that mixtures containing potassium perchlorates and organic fuels can burn flamelessly in a vacuum ($p \sim 10^{-2}$ mm Hg).

Stable flameless combustion of these mixtures depends on the reactions taking place in the reaction layer of the condensed phase with an overall exothermic heat effect; the initial combustion stage (flameless combustion) ends in the formation of a smoke-gas combustible mixture, and then the burning of the latter is completed in the region over its surface until, under certain conditions, the final combustion products are formed.

From this point of view, it is of scientific interest to study the individual stages of the combustion of mixtures containing potassium perchlorate and metal fuels (tungsten, zirconium, and molybdenum) in a vacuum ($p \sim 10^{-2}$ mm Hg), because by means of a vacuum test, it is possible to determine whether the initial combustion stage of the mixture takes place in the condensed phase, or whether the mixture burns only in the gaseous phase. Stoichiometric mixtures containing $KClO_4$ as oxidizer and W, Zn, Mo, and Ti as fuels were used by us as research objects. Grains 5 mm in diameter were compacted to the maximum density.

Table 1 shows the self-ignition temperatures of the mixtures in a vacuum ($p \sim 10^{-2}$ mm Hg) and the sizes of the metal particles.

Table 1

Mixture	Size of metal particles, μ	Temperature of self-ignition, °C
$KClO_4$ + Mo	25—60	$\sim$370
$KClO_4$ + Zr	20—40	$\sim$390
$KClO_4$ + W	<60	$\sim$490
$KClO_4$ + Ti	20—40	$\sim$610

It is seen from the results of the self-ignition temperature of the mixtures that the self-ignition of the mixtures occurs at

temperatures at which metal is in the solid state.

The mixtures studied by us can burn steadily in a vacuum without flame ($p \sim 10^{-2}$ mm Hg) when ignited by a glowing spiral not only at room temperature but also at a temperature below $0°C$: $KClO_4$ + Mo (25—60 μ) and $KClO_4$ + Zr (20—40 μ) burn when the initial temperature of the specimen is $-30°C$, while the mixture $KClO_4$ + W < 60 μ burns when the specimen temperature is $-5°C$. The mixture $KClO_4$ + Ti (20—40 μ) burns steadily in a vacuum ($p \sim 10^{-2}$ mm Hg) if preheated to $200°C$.

Table 2 presents the surface temperatures of the mixtures during flameless combustion in a vacuum ($p \sim 10^{-2}$ mm Hg).

Table 2

Mixture	Size of metal particles, μ	Surface temperature, °C
$KClO_4$ + Mo	25—60	$\sim$610
$KClO_4$ + Zr	20—40	$\sim$860
$KClO_4$ + W	<60	$\sim$850
$KClO_4$ + Ti	20—40	$\sim$640

The surface temperature increases (up to $\sim$ 600—800°C) in mixtures which contain $KClO_4$ and metal as fuels and burn flamelessly due to the overall exothermic process taking place in the reaction layer of the condensed phase of the mixtures.

Table 3

Mixture	Size of fuel particle, μ	Initial temperature, °C	W cm/sec
$KClO_4$ + W	<60	20	$\sim$0.22
$KClO_4$ + W	100 & more	20	$\sim$0.12
$KClO_4$ + Zr	20—40	20	$\sim$0.15

Table 3 presents the results of the determined rate W of flameless combustion of the mixtures.

It is seen, for example, with the mixture $KClO_4$ + W that the rate of flameless combustion of mixtures in a vacuum ($p \sim 10^{-2}$ mm Hg) depends on the size of the fuel particles.

We carried out chemical analyses of the solid and gaseous phases which form during the combustion of mixtures containing potassium perchlorate and W and Zr metal fuels. The solid phase, which is formed during the combustion of mixtures containing $KClO_4$ as oxidizer and tungsten and zirconium as fuels, constitutes $\sim$ 95—97% of the combustion products. The gaseous phase of the mixtures containing $KClO_4$ as oxidizer and metal fuels is made up of the oxygen which does not enter into the reaction with the metal.

Table 4 shows the results of the solid and gaseous phase analysis for flameless combustion ($p \sim 10^{-2}$ mm Hg) in percentages of the initial batch.

Table 4

Mixture	$KClO_4$	KCl	Metal	Metal oxide	O_2
$KClO_4$ + Zr	$\sim$30.2	$\sim$7.0	$\sim$53.1	$\sim$5.3	$\sim$4.4
$KClO_4$ + W	$\sim$17.0	$\sim$5.5	$\sim$63.4	$\sim$10.7	$\sim$3.3

Table 5 gives the percentage of the metal which reacted with the oxygen of the oxidizer ($p \sim 10^{-2}$ mm Hg).

Table 5

Mixture	Percent
$KClO_4$ + Zr	$\sim$7.0
$KClO_4$ + W	$\sim$12.0

Table 6

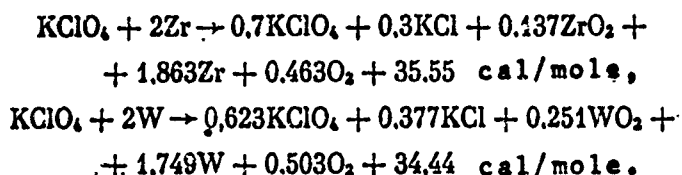| Mixture	Percent
$KClO_4$ + Zr	$\sim$30
$KClO_4$ + W	$\sim$39

Table 6 presents the percentage of the decomposed oxidizer ($p \sim 10^{-2}$ mm Hg).

It is seen from Table 4 that a very small amount of metal oxides is formed during the combustion in a vacuum. When the mixture $KClO_4$ + Zr burns in a vacuum ($p \sim 10^{-2}$ mm Hg), only $\sim$ 7% of the metal reacts with the oxygen of the oxidizer while, under the same conditions, $\sim$ 12% of the metal reacts with the oxygen during combustion of the $KClO_4$ + W mixture.

At the same time, ~ 30% of the oxidizer decomposes with the $KClO_4$ + Zr mixture and ~ 38% with $KClO_4$ + W.

The formation of a small amount of metal oxides during flameless combustion is explained by the fact that the oxidation of metal takes place only on the surface of the particles in the reaction layer of the grain. While in the reaction layer, a part of the oxygen succeeds in reacting with the fuel, whereas another part disperses the condensed substance of the reaction layer and remains unused.

During the combustion of the mixtures containing high-temperature metals investigated by us, such as W, Zr, and Ti, the oxidation of these metals can proceed only on the surface of the fuel particles. The vapor-phase oxidation of these metals is possible in the high-temperature range ($\geq 4000°C$). On the basis of the analysis of the combustion products obtained in a vacuum ($p \sim 10^{-2}$ mm Hg), we formulated decomposition equations for the investigated mixtures, and, by using the heats of formation of the reaction products, we calculated the heat released by the reactions

$$KClO_4 + 2Zr \rightarrow 0.7KClO_4 + 0.3KCl + 0.137ZrO_2 +$$
$$+ 1.863Zr + 0.463O_2 + 35.55 \text{ cal/mole},$$
$$KClO_4 + 2W \rightarrow 0.623KClO_4 + 0.377KCl + 0.251WO_2 +$$
$$+ 1.749W + 0.503O_2 + 34.44 \text{ cal/mole}.$$

In addition, we computed the heats of reaction on the basis of the mean overall specific heat $\bar{C}$, the surface temperature T_{sur}, and the initial temperature T_0. The results are given in Table 7.

Table 7

Mixture	$\Sigma\bar{C}$	T_0, °C	T_{sur}, °C	Q cal/g from formula $Q = \bar{C}(T_{sur}-T_0)$	Q cal/g, from decomposition equation
$KClO_4$ + W	0.076	-5	~850	~65	~68.1
$KClO_4$ + Zr	0.128	-30	~860	~114	~110

As seen from Table 7, the heats of reaction, calculated on the basis of specific heats of the mixtures, the surface temperature T_{sur}, and the initial temperature T_0, coincide well with the heats of reaction calculated on the basis of the heats of formation of the reaction products.

CONCLUSIONS

1. The initial stage of combustion of every mixture occurs in the reaction layer of the condensed phase, i.e., on the surface of the fuel particles, with a total positive heat of reaction, and it ends in the generation of a smoke-gas combustible mixture which then burns in the region above the surface of the mixture until, under certain conditions, the final combustion products are formed.

2. Self-ignition of the mixtures occurs at a temperature at which the metal is in the solid state.

Academy of Sciences USSR, Submitted 13 October 1964
Chemical Physics Institute

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